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Effect of antioxidants on oxidation stability of biodiesel derived from vegetable and animal based feedstocks

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ABSTRACT

The increase of energy demand coped with utilization of fossil resources have engendered serious environmental impact. The progressively stringent worldwide emission legislation and increasing greenhouse gas emission require significant research effort on alternative fuels. Therefore, biodiesels are becoming important increasingly due to its ease in adaptation, environmental benefits and prospect in energy security. Biodiesel derived from vegetable oils, waste cooking oils and animal fats are long chain fatty acid alkyl esters, which contains unsaturated portions that are susceptible to oxidation. Biodiesel oxidation is a complex process having a number of mechanisms involved. Autoxidation radical chain reactions are the primary cause of biodiesel degradation that leads to formation of hydroperoxide, which, after that decompose to form an array of secondary oxidation products like aldehydes, ketones, carboxylic acids, oligomers, gum, sediment etc. Antioxidants are often used to inhibit biodiesel oxidative degradation. The present review attempts to cover the inhibition action of natural and synthetic antioxidants, methods used to analyze biodiesel oxidation and their effect on biodiesel derived from various feedstocks. Phenolic antioxidants are more effective compared to amine antioxidants. Pyrogallol is found to be the most effective antioxidant to improve the oxidation stability in case of almost all biodiesels reviewed.

Contents

Abbreviations: AO/AH, antioxidant; AOCS, American Oil Chemists' Society; BHT, butylated hydroxytoluene; BHA, butylated hydroxyanisole; CSOME, cottonseed oil methyl ester; CA, caffeic acid; DTBHQ, 2,5-di-*tert*-butyl-1,4-dihydroxybenzene; DPD, *N,N′*-diphenyl-*p*-phenylenediamine; EHN, 2-ethylhexyl nitrate; FA, feluric acid; FAAE, fatty acid alkyl ester; FAME, fatty acid methyl ester; FFA, free fatty acid; FTIR, Fourier transform infrared; h, hour; IB, Ionol BF200; IP, induction period; IPR, relative change in IP; MD, metal deactivator; NMR, nuclear magnetic resonance; OBPA, octylated butylated diphenyl amine; OS, oxidation/oxidative stability; OSI, oil stability index; OT, onset temperature; PDSC, pressurized differential scanning calorimetry; PG, propyl gallate; PY, Pyrogallol; TBHQ, *tert*-butylhydroxyquinone; TG, thermo gravimetric; UFOME, used frying oil methyl ester; YGME, Yellow grease methyl ester; α-T, α-Tocopherol

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1. Introduction

The replacement of fossil fuel-derived energy is one of the most pressing technological issues nowadays [1]. The detrimental impact on environment due to burning of fossil fuel, the unsteadiness in both demand and supply of fuels, and the rising cost of production of petroleum products are intensifying this issue. Thus, biofuels especially biodiesels are receiving significant attention because of these environmental as well as energy concerns [2–4]. The use of biodiesel is becoming popular due to its adaptation with current transportation infrastructure and requires minimal modification for its use [5,6].

Biodiesel, which refers to the fatty acid alkyl esters (FAAEs), are derived from lipid substances originated from vegetable oil, animal fats, waste greases, recycled cooking oils etc. In order to produce biodiesel, vegetable oils of edible source were treated as one of the potential feedstocks. However, due to criticism on edible-based oil use for fuel production, other sources e.g. non-edible oils of plant origin, waste fats with high free fatty acid (FFA) content etc. are now being used for biodiesel production. Researchers are also in quest for newer feedstock of biodiesel production [7–19]. Triglyceride molecules that are the main constituents of these oils are tranesterified with addition of alcohols, for example, methanol in presence of a suitable catalyst to form FAAE [10,13,20–27]. The fatty acid profile i.e. the chain length and the level of unsaturation of the produced FAAE corresponds to that of parent oil [28]. It is the fatty acid profile, which influences the physicochemical properties of biodiesel.

Fuel instability is the susceptibility of fuel to degradation processes by alteration of fatty acid composition that form undesirable species. Although biodiesel is thermodynamically stable, its instability primarily occurs from contact of oxygen present in the ambient air that is referred to as oxidative instability. The term 'oxidation stability'(OS) is a general term, which differs from 'storage stability' and 'thermal stability', as the oxidative degradation may occur during extended storage period, transportation and end use [29]. Other instabilities of the fuel could occur if the fuel is exposed to air and/or light, experience higher temperature and if the presence of metallic compound incites catalytic degradation process. During shipping and use in transport vehicles, biodiesel come across different fuel line components, namely, fuel tank, feed pump, fuel lines, fuel filter, fuel pump, fuel injector cylinder, piston assembly, etc. which are made of various transition metals and elastomers [30,31], shows prooxidant behavior on it. As the oxidation occurs to biodiesel, a series of changes in its properties occurs. Properties like the density, kinematic viscosity, acid value, and peroxide value increase, while the iodine value and methyl esters content decrease [32]. Accelerated oxidation of biodiesel also results in an increase in polymer content that initiates the gum and sediments formation. It influences the corrosion of engine components, too through which the fuel comes in contact up to combustion chamber like injector, piston ring, piston liner, etc. [29,33–35]. Other physicochemical properties that are sensitive to biodiesel oxidation include cetane number, flash point, refractive index, and di-electric constant [36–38]. Biodiesel admixed in the lubricating oil during crankcase dilution tends to be persistent within it due to less volatility and begins to degrade and oxidize. This causes a significant increase in viscosity of the sump oil, thereby, resulting the decrease of performance, greater engine wear and necessitates a premature oil change [39].

Oxidation stability of biodiesel has been a subject of considerable research for last two decades [40–50]. Numerous methods, including various physicochemical properties like induction period, viscosity, iodine value, peroxide value and acid value monitoring, analyzing the methyl ester content, thermo gravimetric (TG) and pressurized differential scanning calorimetry (PDSC), nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), etc. have been applied in oxidation stability studies of biodiesel [32,51–55]. Several published articles focused on stability of biodiesel [46,56–62] without using antioxidants by monitoring the physicochemical properties which generally recommended the use of antioxidants for good storage stability. Some of the published articles also studied the stability of blends of biodiesel along with diesel [63–65]. The interesting part of antioxidants action is that its action depends on the fatty acid methyl ester (FAME) composition [66,67]. Previous reviews [37,68–70] on oxidation stability of biodiesel was focused on detailed discussion on oxidation mechanism, characterization of stability, effects of biodiesel oxidation in diesel engine operation and emission with little discussion on antioxidant chemistry. Hence, this article attempts to review the antioxidant inhibition mechanism on biodiesel and its effect on oxidative and storage stability of biodiesels derived from various feedstocks.

2. Oxidative degradation chemistry

Biodiesels are more susceptible to degradation compared to fossil diesel because of the presence of unsaturated fatty acid chain in it (carbon double binds C=C) [37,71]. The mechanisms of degradation are: (a) autoxidation in presence of atmospheric oxygen; (b) thermal or thermal-oxidative degradation from excess heat; (c) hydrolysis in presence of moisture or water during storage and in fuel lines; and (d) microbial contamination from contact with dust particles or water droplets containing fungi or bacteria into the fuel [37,38,49]. This degradation is exasperated if there is at least two or higher number of carbon double bonds (polyunsaturation) are extant in their fatty acid chains [72]. More than half of a century has been elapsed after the establishment of autoxidation mechanism of polyunsaturated fatty acids as a radical chain reaction [73–75]. This was followed by interpretation on role of antioxidants as inhibiting agent [76].

Biodiesels are comprised of mainly fatty acid chains converted to corresponding esters. Almost all plant-derived oils composed of polyunsaturated chains, which contain allylic and bis-allylic sites [32], which are methylene ($-CH_2-$) interrupted chains [36]. The result of oxidation process of biodiesel is formation of hydroperoxides. Within this process, three partially overlapping phases of radical reactions can be distinguished: initiation, propagation and termination (Fig. 1). The initiation phase forms and expands the pool of carbon centered lipid radical, which is formed by abstraction of a methylene hydrogen atom from polyunsaturated fatty acids (LH/RH) by free radicals and other reactive species (e.g. metals) [77]. Following the initiation, this radical cycles between the fatty acyl (pentadienyl) radical $L^{\bullet}$ and the peroxyl radical ($LOO^{\bullet}$) (Fig. 1). Hydroperoxide (LOOH/ROOH) is formed after completion of propagation phase where the polyunsaturation has been isomerized to include a conjugate diene, which is produced from intrusion of oxygen and the fatty acid into the cycle. The peroxyl radical continues to give the hydroperoxide by inclusion of hydrogen atom from a new molecule of fatty acid (LH/RH). This in turn becomes a pentadienyl radical ($L^{\bullet}$) which is ready to pick up oxygen to form the next peroxyl radical. Once the hydroperoxides are formed, they are decomposed and then inter-react to form numerous secondary oxidation products. These consist of higher molecular weight oligomers are often termed as polymers. Termination occurs when non-radical products are formed by reaction between two radicals, or when an antioxidant (AH) reduces the peroxyl to a hydroperoxide while transforming itself into a stable radical ($A^{\bullet}$). However, termination phase could occur without presence of antioxidants happens only if the concentration of radicals is sufficient so that there is high probability of two radicals actually colliding [78].

The susceptibility to oxidation of a biodiesel increases with the number of double bonds, their relative location, and degree of conjugation of double bonds present [79,80]. Therefore, the more the amount of unsaturated fatty acid chains in the biodiesel the more it is more prone to oxidation. The bis-allylic positions in polyunsaturated fatty acid, such as linoleic acid (C18:2) (double bonds at Δ9 and Δ12, giving one bis-allylic position at Δ11) and linolenic acid (C18:3) (double bonds at Δ9, Δ12, and Δ15, giving two bis-allylic positions at Δ11 and Δ14), are even more prone to oxidation than allylic positions. The oxidation stability of unsaturated methyl esters decreases according to the order of linolenic, linoleic, oleic (C18:1), and relative rates are 98:41:1 [29].

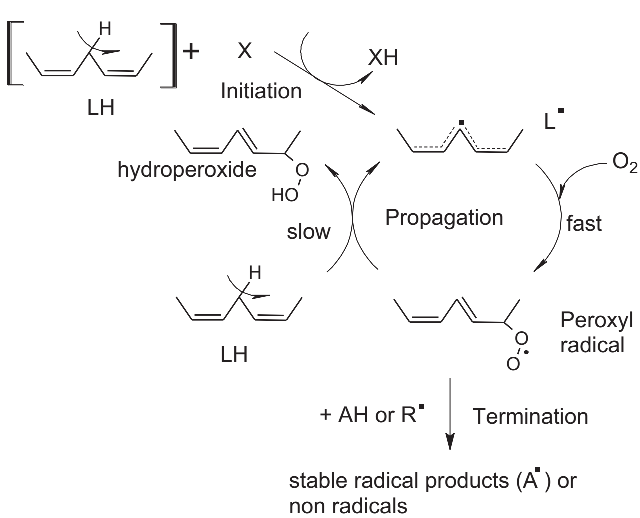


Fig. 1. Three phases of the autoxidation process (Adopted in modified form from Ref. [82]).

In case of thermal oxidative degradation, high temperature induces molecular isomerization of fatty acid chains. Two types of isomerization are possible: (a) positional isomerization of unsaturated bonds lead to formation of reactive conjugated and bis-allylic configuration; (b) conformational *cis*/*trans* isomerization. It is to be noted that, while a single *trans*-unsaturation is more stable than a *cis*-unsaturation, conjugated *trans*-unsaturation is more sensitive to oxidation than neighboring *cis*-unsaturation [81].

The oxidative or thermal degradation of biodiesel could be divided into two stages [68]. In the first stage, lower molecular weight compounds are produced in the biodiesel. Later, in the second stage, higher molecular-weight species are formed ensuing an increases of fuel viscosity as well as solid deposits [83]. Fang and McCormick [84] studied the degradation pathways of methyl esters under accelerated conditions with soy methyl ester using NMR, FTIR and gravimetric measurement of deposit formation. To simulate accelerated oxidation radical initiator 2-ethylhexyl nitrate (EHN) (2 wt%) was added and subjected to heat. They proposed four possibilities of degradation: (a) autoxidation/peroxidation; (b) reverse transesterification of methyl esters; (c) interaction of methyl ester with hydroperoxides; and (d) hydrolysis of esters. After the peroxyl radical formation (Fig. 1) two different pathways were proposed in this research. First one is through cyclical formation of peroxide decomposed into aldehydes, ketones and acids which than forms oligomers. The second one is through intermolecular interaction to form dimers and larger oligomers. During the early stages of oxidation, the concentration of hydroperoxide (LOOH) remains very low until a time interval has elapsed. This time interval is referred to as "induction period (IP)". Once the IP has elapsed, the LOOH level quickly increases, signaling the onset of rapid oxidation [85].

3. Antioxidant chemistry

Antioxidants significantly slow down the biodiesel degradation process. According to their mode of action, antioxidants could be classified in to various groups: free radical terminators, metal ion chelators capable of catalyzing lipid oxidation, or as oxygen scavengers that react with oxygen in closed systems [86]. Free radical terminators are considered primary antioxidants, which react with high-energy lipid radicals and convert them into thermodynamically more stable products. Phenolic antioxidants (AH) are recognized as free radical terminators and these are mostly used antioxidants. Secondary antioxidants work by impending the rate of chain initiation by decomposing the hydroperoxides. The mechanism of action of free radical terminators are discussed here.

The first study on activities or reaction mechanism of antioxidant was conducted by Bolland and Ten Have [87] where they postulated reaction (1) and (2) as the mechanisms of action of free radical terminators. The free radical terminators contain a highly labile hydrogen, which is rapidly donated to peroxyl radical which interfere with lipid oxidation process (reaction (1) and (2)) [88]. The latter reactions (reactions (3) and (4)) compete with the chain propagation reaction (Fig. 1).

$$ROO^{\bullet} + AH \rightarrow ROOH + A^{\bullet} \quad (1)$$

$$RO^{\bullet} + AH \rightarrow ROH + A^{\bullet} \quad (2)$$

$$ROO^{\bullet} + A^{\bullet} \rightarrow ROOA \quad (3)$$

$$RO^{\bullet} + A^{\bullet} \rightarrow ROA \quad (4)$$

These reactions are exothermic in nature. As the bond dissociation energy of 'A–H' and 'R–H' increases, the activation energy of these reaction increase. Therefore, as the bond strength of 'A–H' decreases, the efficiency of antioxidant increases. Moreover,

Table 1
Physicochemical properties of different antioxidants [95,96].

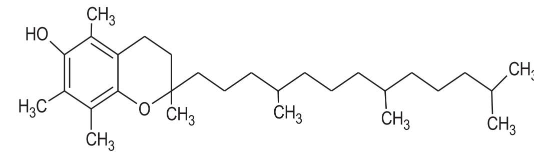
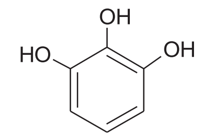
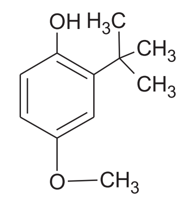
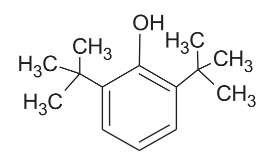
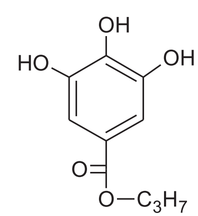
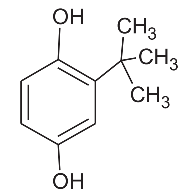
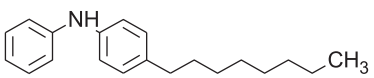
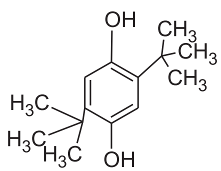
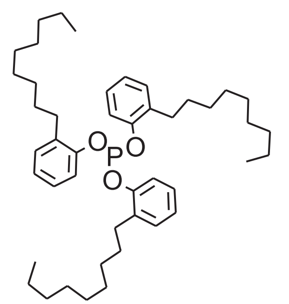
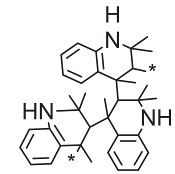
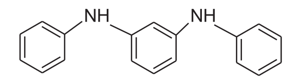
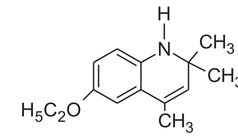
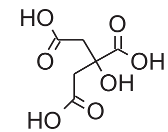
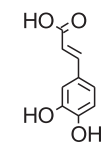
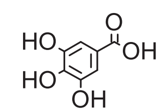
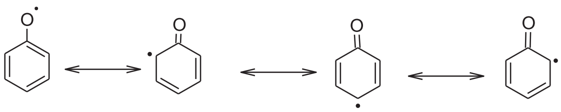
Antioxidants	Type	CAS number	Molecular formula	Molecular weight (g/mol)	Water solubility	Melting point (°C)	Boiling point (°C)	Structure and IUPAC name	Ref.
α-Tocopherol	Natural	59-02-9	$C_{29}H_{50}O_2$	430.71	Insoluble	2.5–3.5	200–220 (0.1 mmHg)		[88]
Pyrogallol (PY)	Phenolic	121-79-9	$C_{10}H_{12}O_5$	212.2	/	150	Decompose	 benzene-1,2,3-triol	[88]
Butylated hydroxyanisole (BHA)	Phenolic	25103-16-5	$C_{11}H_{16}O_2$	180.24	Insoluble	48–55	264–270	 2-*tert*-butyl-4-methoxyphenol	[88]
Butylated hydroxytoluene (BHT)	Phenolic	128-37-0	$C_{15}H_{24}O$	220.35	Extremely low solubility 1.1 mg/L (20 °C)	70–73	265	 2,6-di-*tert*-butylphenol	[88]
Propyl gallate (PG)	Phenolic	87-66-1	$C_6H_6O_3$	126.11	/	131–134	309	 propyl 3,4,5-trihydroxybenzoate	[88]

Table 1 (*continued*)

Antioxidants	Type	CAS number	Molecular formula	Molecular weight (g/mol)	Water solubility	Melting point (°C)	Boiling point (°C)	Structure and IUPAC name	Ref.
Tert-butylhydroxyquinone (TBHQ)	Phenolic	1948-33-0	$C_{10}H_{14}O_2$	166.22	Slightly soluble	127–129	273	 2-*tert*-butylbenzene-1,4-diol	[88]
Octylated butylated diphenyl amine (OBPA)	Amine	4175-37-5	$C_{20}H_{27}N$	281.43508	Slightly soluble		409.302	 4-octyl-*N*-phenylaniline	[97]
2,5-di-*tert*-butyl-1,4-dihydroxybenzene (DTBHQ)	Phenolic	88-58-4	$C_{14}H_{22}O_2$	222.323303		216–218	334.406	 2,5-di-*tert*-butylbenzene-1,4-diol	[98]
Tris (nonylphenyl) phosphate (Naugard P)	Phosphite	26523-78-4	$C_{45}H_{69}O_3P$	689.00			> 360	 **Tris (2-nonylphenyl) phosphite**	[98]

Poly(1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK)	Amine	26780-96-1	$C_{12}H_{17}N$		Insoluble	355	132 (13 Torr)		[98]
N,N′-diphenyl-p-phenylenediamine (DPD)	Amine	5905-36-2	$C_{18}H_{16}N_2$	260.33304			435.6	 *N,N'*-diphenylbenzene-1,3-diamine	[99]
Ethoxyquin	Amine	91-53-2	$C_{14}H_{19}NO$	217.30679	< 0.1 g/100 mL at 20 °C	< 0	123–125	 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	[100]
Citric acid		77–92-9	$C_6H_8O_7$	192.124	73 g/100 ml	153–159	310	 2-hydroxypropane-1,2,3-tricarboxylic acid	[100]
Caffeic acid (CA)	Phenolic	331-39-5	$C_9H_8O_4$	180.16		211–213	416.817	 (2*E*)-3-(3,4-dihydroxyphenyl)prop-2-enoic acid	[101]
Gallic acid (GA)	Phenolic	149-91-7	$C_7H_6O_5$	170.12	1.19 g/100 mL	260	501.104	 3,4,5-trihydroxybenzoic acid	[38]

ensuing phenoxy radical itself should not proceed to initiate a new free radical or it should not be subjected to oxidation chain reaction [89,90]. In this case, phenolic antioxidants are very good option as they are good hydrogen donors in addition to their relatively stable radical intermediates because of resonance delocalization as well as lack of apt sites to be attacked by molecular oxygen. The stabilization of phenoxy radical occurs by delocalization of unpaired electrons around the aromatic ring, as indicated by the valance bond isomers (reaction 5).


(5)

Phenol itself is chemically inert as an antioxidant. Hydrogen substitution by alkyl groups in *ortho*- and *para*-position increases the density of electron of the OH moiety by inductive effect. This enhances its reactivity toward lipid radicals. Moreover, enhancement of the antioxidant activities are observed when the ethyl or n-butyl groups are substituted than the methyl groups at the *para*-position [91]. Bulky groups at *ortho*-position also increases the stability of the phenoxy radical as in BHA (Table 1) [92]. These substituents intensify the stearic hindrance in the region of the radicals as well as decrease the rate of possible propagation reactions (reactions (6)–(8)) that may occur.

$$A^{\bullet} + O_2 \rightarrow AOO^{\bullet} \quad (6)$$

$$AOO^{\bullet} + RH \rightarrow AOOH + R^{\bullet} \quad (7)$$

$$A^{\bullet} + RH \rightarrow AH + R^{\bullet} \quad (8)$$

The entrance of second OH group at the *ortho*- or *para*-position of the existing hydroxyl group of phenoxy radicals increases its antioxidant activity by stabilization through an intermolecular hydrogen bond (Fig. 2).

Butylated hydroxytoluene (BHT) and Butylated hydroxyanisole (BHA) are most common monohydric phenolic antioxidants (Table 1). BHA is found commercially as white waxy flakes and that of BHT as white crystalline compound [86]. Both of these antioxidants are strongly soluble in fats and are insoluble in water. Moreover, since both of these are mono-phenols, they can yield radical intermediates with moderate resonance delocalization. The *tert*-butyl groups of BHT do not usually permit the involvement of yielded radical in other reactions [93]. Therefore, a lipid peroxyl radical might join with the BHT molecule as shown in reaction (9) (Fig. 3).

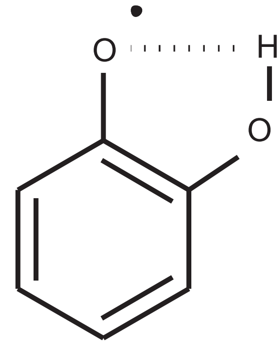
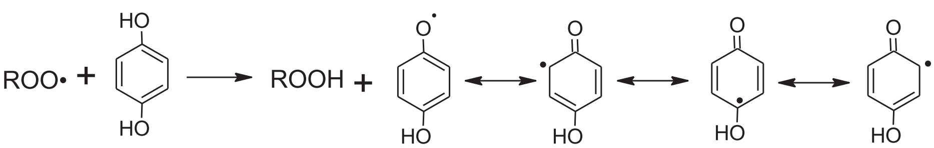
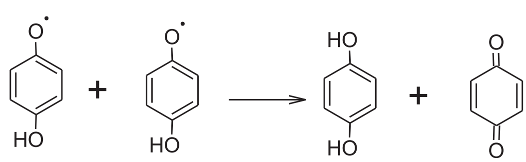
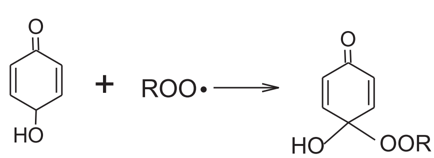


Fig. 2. Stabilized phenoxy radical.

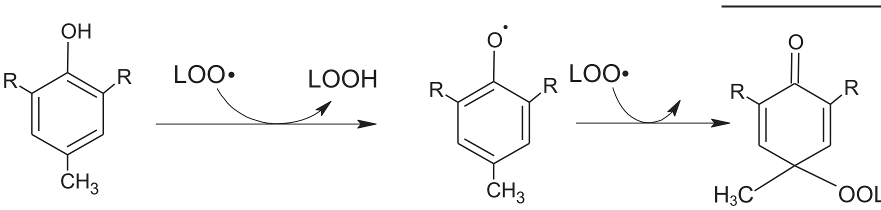
Tert-butylhydroxyquinone (TBHQ) is commercially available as beige-colored powder, which provides a good carry-through protection. It is adequately soluble in fats. Since, it is a diphenolic antioxidant; it can react with peroxyl radicals forming semiquinone resonance hybrid. The semiquinone radical intermediates may undergo different reactions and consequently form more stable products. They also can react with one another to produce dimers, dismutate, and regenerate semiquinone. Even the reaction can occur with another peroxyl radical, as shown in reactions (10)–(12).


(10)


(11)


(12)

Based on their labile hydrogen the phenolic antioxidants can be ranked as BHA ≈ BHT < DTBHQ ≈ TBHQ < PG ≈ PY which is applicable to some edible oil based biodiesel. Another important antioxidant type is amine type that also falls in the group of free radical terminators. The mechanism of antioxidant action is shown


R = *tert*-butyl
(9)

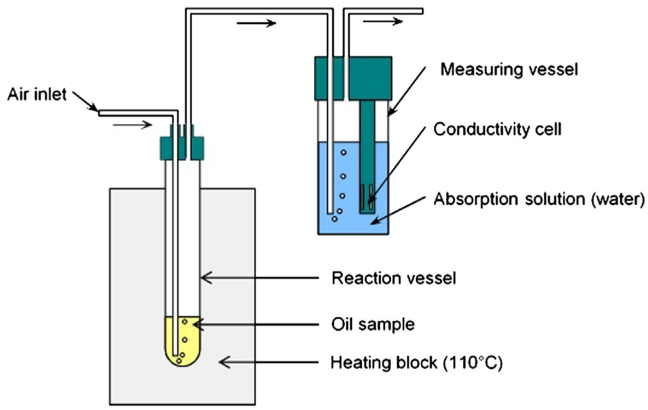
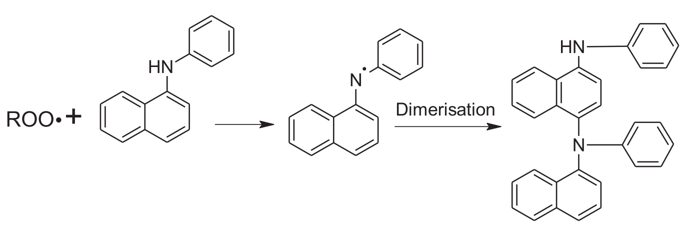


Fig. 3. Principle of Rancimat instrument.

in reaction (13).



(13)

The effect of antioxidant concentration on autoxidation rates depends on many factors, including the structure of the antioxidant, prevailing storage conditions, and the nature/composition of the sample being oxidized [86]. The term, "Stabilization factor" is often used to denote the effectiveness of an antioxidant where, $F = IP_x/IP_o$, where IP_x is known as induction period when the antioxidant is present and IP_o is regarded as induction period when the antioxidant is absent [94]. Table 1 contains physicochemical properties of commonly used antioxidants and their structure.

4. Stability testing standard

The methodology of determining the oxidative stability mostly based on the similar methodology as of accelerated tests, which was originally suggested by Hadorn and Zürcher [102] to monitor the rancidity of edible oils, known as the Rancimat method [51]. This method has been considered as the standard stability test method for measuring the oxidation stability of biodiesels in both EN 14214 and ASTM D 6751 [103]. One of the key steps of the test is measuring the increment of the conductivity of deionized water confined in the reservoir. Volatile acids are retained in the reservoir, too as emancipated during the propagation of the oxidation process of the fatty acid compounds. In practice, the oxidation process of biodiesel is prompted by passing air at a flow rate of 10 L/h through a specified amount of sample (3 g) kept at 110 °C and then through 50 ml deionized water in a measuring vessel. The sample is kept at 110 °C to simulate the accelerated oxidation. Water absorbs the volatile oxidation products (mainly formaldehyde and short-chain acids) which causes an increase in conductivity. A set of electrode is inserted in the water that is connected to a measuring and recording device. By continuously recording the conductivity and plotting them, an 'oxidation curve' is obtained whose point of inflection (tangential intersection point) is known as the IP [104,105]. In order to determine the induction time automatically, the second derivative of the obtained curve is executed. A method nearly identical to Rancimat method is Oil Stability Index (OSI) method that is an AOCS (American Oil Chemists' Society) acknowledged index for this case, which has been used in earlier studies [29,106–108].

5. Antioxidant inhibition effect on different biodiesels

Inhibition effect of antioxidants depends on the composition of fatty acid methyl esters. The higher the content of polyunsaturation the higher it is prone to oxidation. The percentage amount of both saturated and unsaturated contents of different biodiesels is shown in Table 2. The inhibition effect of various antioxidants on biodiesel derived from different feedstocks is discussed in the following sections.

5.1. Soybean based biodiesel

Damasceno et al. [101] studied the effect of three antioxidants namely caffeic acid (CA), feluric acid (FA) and TBHQ using three accelerated techniques: Rancimat, PetroOXY and PDSC on soybean based ethyl ester with initial IP of 4.34 h. All antioxidants were added at 1000 ppm. It was found that only CA was able to meet EN 14214 specification after 90 days of storage period.

Santos et al. [109] studied the effect of CA, BHT and TBHQ at varying concentration on soybean biodiesel with initial IP of 1.72 h in presence of 2 ppm of copper, chromium, iron, cobalt and manganese salt. Among the three antioxidants, 1000 ppm of CA was able to meet EN 14214 limit.

Serrano et al. [110] studied the effect of four different commercial antioxidants at 1000 ppm and two different purification steps on soybean based biodiesel. Among the four, two were BHT based (AO1, AO2), one PG based (AO3) and one is tocopherol based (AO4). Two different purification steps were used for removal of impurities of methyl ester phase: a) using distilled water and b) using citric acid solution. They observed citric acid washed biodiesel met EN 14214 specification but water washed sample failed. They also observed reduced "relative change in IP" (IPR) values of biodiesel subjected to storage for citric acid washed biodiesel compared to water washed one. Antioxidants AO3 and AO4 were able to meet EN 14214 standard even after 6 months regardless of the use of washing step.

In another study, Serrano et al. [100] explored same feedstock with same antioxidants with varying concentration and same purification step as above. The IP for water washed and citric acid washed samples were 2.9 and 6 h respectively. AO4 at all ppm were able to meet EN specification in case of water washed biodiesel. Except AO1 rest were able to meet EN specification at all concentration in case of citric acid washed biodiesel. However, AO3 provided best results.

Maia et al. [129] studied the efficiency of synthetic antioxidants on soybean biodiesel using simplex-centroid mixture experimental design. Besides, the storage time and the oxidation reaction at various temperatures were estimated and monitored respectively by the researchers in presence of antioxidants. They concluded that BHA, TBHQ as well as BHT act in a dissimilar way depending on the temperature. On the other hand, both BHA and TBHQ exhibit higher efficiency to avert the oxidation of biodiesel.

Fernandes et al. [111] studied the influence of the antioxidant TBHQ on the storage stability of metal contaminated biodiesel. Metallic coupons were prepared from both galvanized steel as well as carbon steel immersing in biodiesel for different exposure time following ASTM method. The initial IP of the biodiesel sample was 7.8 h, which was increased to 10.5 h by adding 500 mg/kg TBHQ. After 12 weeks of storage, biodiesel exposed to both materials failed to meet IP values of EN specification. However, antioxidant added samples presented IP of about 8 h after 84 days. Presence of

Table 2
Saturated and unsaturated percentage of biodiesels (wt%).

Biodiesel	Saturated (wt%)	Mono unsaturated (wt%)	Poly unsaturated (wt%)	Total unsaturated (wt%)	Ref.
Soybean	14.5–19.0	24–25.6	55.5–61.3	80.2–85.3	[88,98,100,101,109–112]
Rapeseed	4.7–7.5	50.6–59.1	32.6–34.1	85.5–91.7	[99,100,110,113]
Jatropha	21.1–24.5	39.1–44.5	34.4–36.2	75.3–78.9	[64,114–116]
High oleic Sunflower	7.9	83.1	9.1	92.2	[100,110]
Sunflower	11.1	25.6	63.3	88.9	[98]
Safflower	8.6	13.9	76.2	89.1	[99,117]
Canola	5.4–6.5	65.3–67.8	26.7–28.3	93.6–94.5	[88,98]
Palm	43.4–50.6	40.2–45.2	7.9–12.2	53.1–54.0	[99,100,110,116,118]
Cottonseed	25.9–28.2	15.5–18.9	53.0–57.9	71.8–73.4	[119–121]
Castor	1.53	90.7	5.6	96.3	[12]
Pongamia/Karanja	16–17.1	68.7–72.2	1.5–11.8	80–84.0	[38,116,122–124]
Croton	9.6	11.8	78.5	90.3	[125]
Terminalia belerica	16.3–39.5	31.8–61.5	18.5–28.8	80	[17,126]
Linseed	11.4	21.8	66.2	88	[127]
Açaí	27.5	57	9	66	[127]
Recycled cooking oil	15.52–18	30.6–38.65	45.63–51.3	81.9–84.82	[94,112,128]
Animal fat	28.4–39.96	37.28–47.1	10.4–28.4	57.5–71.6	[66,88,112]
Grease	20.2–30.9	31.4	48.4	62.8–79.8	[120]

TBHQ mitigated the corrosion of coupons, which is supported by absence of zinc after 12 weeks.

Yang et al. [88] studied the effect of TBHQ, PY, PG, BHA, BHT and α-T on one soybean methyl ester with spiking concentration ranged from 0 to 8000 ppm. The initial IP of this sample was only 0.7 h. PY provided the greatest enhancement below 3000 ppm and TBHQ provided this above 3000 ppm. The order of effectiveness for this case was TBHQ > PY > PG > BHA > BHT. PY, TBHQ and PG with concentrations of 1500, 3000 and above 6000 ppm respectively, were able to meet EN14112 standard. The rest failed to provide IP of 6 h even at 8000 ppm. Again, they investigated on another sample with original IP of 4.8 h. They mixed varying concentrations of PY (50–500 ppm) in 5% (mass/mass) copper and lead adulterated sample. About 50 ppm of PY was sufficient to reach the EN specification for pure biodiesel. Copper and lead adulterated sample had an IP of less than 1 h. At 500 ppm spiking concentration, the IP value of these samples conformed to EN standard.

Focke et al. [98] studied the inhibition activity of DTBHQ on this biodiesel with initial IP of 3.3 h. They found that the oxidation stability is decreased with addition of a low level of DTBHQ in the biodiesel. However, after 0.2 wt% concentration IP started to increase and doubled at 0.5 wt% and tripled at 1 wt%. Ryu [130] studied the effect of five different antioxidants (BHA, BHT, TBHQ, PG and α-T) with added quantity of 0, 100, 300, 500, 1000 and 2000 ppm on this biodiesel with initial IP of 1.36 h. BHA, BHT at 1000 ppm was able to provide sufficient resistance to oxidation to meet EN specification. In case of TBHQ and PG, this amount was less than 300 ppm. The order of efficiency was TBHQ > PG > BHA > BHT > α-T.

Tang et al. [121] investigated the effectiveness using eight antioxidants (α-T, BHA, BHT, TBHQ, Ionol BF200 (IB), PG and PY) individually to ameliorate the IP of soybean based biodiesel (SBO biodiesel) for various concentration between 250 and 1000 ppm. Commercially available SBO-biodiesel with initial IP of 3.52 h was used here. Among them PY was found to be most effective antioxidant with PG to be the second best at a concentration below 1000 ppm. However, at 1000 ppm TBHQ produced better result compared to TBHQ in term of increasing IP. At 1000 ppm BHA, BHT and DTBHQ increased IP to meet EN specification. Distilled Soybean based biodiesel without antioxidant showed much lower oxidative stability (0.77 h). With this biodiesel, TBHQ achieved best result with stabilization factor of 15 at 1000 ppm. Both BHA at 500 ppm and PY at 1000 ppm improved the IP to meet En14214 specification. The order of effectiveness was TBHQ > BHA > PY > BHT > DTBHQ > PG > IB > α-T.

Domingos et al. [131] studied the effect of BHT, BHA and TBHQ on soybean oil ethyl ester with initial IP of 0.16 h at various concentration ranging from 200 to 8000 ppm. The greatest stabilization was obtained with 8000 ppm of TBHQ (52.53). BHT provided stabilization factor of 35.59 at 8000 ppm. In case of BHA with was only 1500 ppm with factor of 8.18. At and above 2000 ppm BHA did not show any inhibition action or even displayed some pro-oxidation behavior. To investigate the synergistic effect of different antioxidants, they applied a factorial design with these antioxidants. Surprisingly they found pro-oxidant behavior at the tested levels compared to behavior shown by individual antioxidants.

Lapuerta et al. [112] studied the effect of test temperature (110–130 °C) and different BHT concentrations on soybean based biodiesel with initial IP of 3.61 h. From 1300 to 17000 ppm of antioxidant was required to meet the current EN14214 standard at different test temperatures.

Dunn [132] reported increased activity i.e. increased IP with increasing antioxidant loading (concentration). However, sharp increase in IP at lower loadings (less than 1000 ppm) and smaller increase at higher loadings (2000–5000 ppm) were observed. BHA to be the most effective antioxidant interpreted from OT (onset temperature). Phase equilibrium studies were carried out to test the physical compatibility i.e. solubility of antioxidants and found that PG has relatively poor solubility in vegetable oil derivatives.

5.2. Rapeseed based biodiesel

Serrano et al. [110] studied the effect of four different commercial antioxidants at 1000 ppm and two different purification step on rapeseed based biodiesel as described in previous section. They observed citric acid washed biodiesel met EN 14214 specifications whereas water washed sample failed. However, higher IPR was observed for it when subjected to storage. Antioxidant AO3 & AO4 were able to meet EN 14214 standard after 6 months regardless of the use of washing step. In another study, Serrano et al. [100] explored same feedstock with same antioxidants at varying concentration and same purification step as described in Section 5.1. The IP for water washed and citric acid washed samples were 4.6 and 8.1 h, respectively. Both AO1 and AO4 at all concentration were able to meet EN specification in case of water washed biodiesel. All the antioxidants were able to meet EN specification at all concentration in case of citric acid washed biodiesel. However, except AO3, rest did not produce any significant improvement. To study the effect of citric acid as metal deactivator they added varying

copper concentration in biodiesel and found that citric acid washed biodiesel prevented the destabilization of biodiesel.

Xin et al. [99] studied the effect of PG and DPD (Table 1) at various concentrations. They exposed the rapeseed biodiesel with initial IP of 6.5 h to supercritical methanol at 270 °C/17 MPa for 30 min and compared it with unexposed one. Sample with PG and exposed to supercritical methanol produced better result compared to unexposed PG and DPD doped and exposed biodiesel. Sendzikiene et al. [113] studied the effect of synergistic mixture of BHA and 20% w/w citric acid as well as BHT and 20% w/w citric acid at various concentrations from 200 ppm to 1000 ppm on rapeseed methyl ester. The optimal concentration for both antioxidant mixtures was 400 ppm.

5.3. Jatropha based biodiesel

Jain and Sharma [104] added PY at varying concentration (200, 400, 600 and 800 ppm) to jatropha biodiesel (JBD) and found that after six months of storage all retained IP over 6 h. In another study, Jain and Sharma [64] tried to optimize the antioxidant concentration of five different antioxidants (PY, PG, BHA, BHT and TBHQ) to cope with the EN 14214 specification in case of JBD with IP of 3.27 h. PY at 100 ppm; PG and TBHQ at 300 ppm; BHT at 400 ppm and BHA at 500 ppm was able to reach that specification.

Sarin et al. [122] conducted a study about the effect of three antioxidants namely BHT, bis-2,6-ditertiarybutyl phenol derivative, and OBPA (Table 1) on different metal contaminated samples of JBD. The metals were iron, nickel, manganese, cobalt and copper those are usually found in the metallic containers. They found copper had strong catalytic effect and small concentrations of metals had nearly the same effect on stability as large amount. In order to obtain the optimum antioxidant quantity, they added 2 ppm of metal contaminants. For iron and nickel minimum 500 ppm, for manganese minimum 700 ppm, for cobalt minimum 900 ppm and for copper 1000 ppm of BHT are required to meet EN14214 specification. As a continuation of previous study, Sarin et al. [114] studied the synergistic effect of both metal deactivators (MD) as well as synthetic antioxidants on metal contaminated JBD sample. 5 ppm and 10 ppm of *N*,*N′*-dialicylidene-1,2-diaminopropane along with different concentration of BHT were added to those samples as described earlier. They found reduction of usage of BHT for both the cases. Therefore, the researchers finally commented that there could be an effective reduction of using antioxidants by doping small amount of MD in the metal contaminated biodiesel.

Sarin et al. [116] studied four antioxidants namely BHT, bis-2,6-ditertiarybutyl phenol derivative, mixed butylated phenol and amine antioxidant OBPA. All of these antioxidants were added at an amount of 25 ppm to 400 ppm with the JBD of initial IP 3.23 h. They found that 200 ppm of BHT sufficiently meet the EN14214 standard. Again, they blended jatropha and palm at various proportions to increase the IP of jatropha biodiesel and found that 60% of palm biodiesel should be mixed with JBD to cope with EN 14214 specification.

5.4. Sunflower based biodiesel

Serrano et al. [110] performed study with four different commercial antioxidants each of at 1000 ppm and two different purification step on rapeseed based biodiesel as described in Section 5.1. They observed citric acid washed biodiesel met EN 14214 specifications whereas water washed samples failed. All the antioxidants were able to meet EN 14214 standard after 6 months regardless of the use of washing step. In another study, Serrano et al. [100] explored same feedstock with same antioxidants at varying concentration and same purification step as described in Section 5.1. From their observations, the IP for water washed and citric acid washed samples were 5.1 h and 14.4 h, respectively. AO4 and AO3 were most effective in case of water washed and citric acid washed samples respectively.

Focke et al. [98] conducted the study to determine the influence of 3 different types of antioxidants on sunflower biodiesel with initial IP of 0.61 h. The added antioxidants were of phenolic (DTBHQ), phosphite (Naugard P) and amine (Orox PK) types (Table 2). They found amine type as the best antioxidant for sunflower derived biodiesel. At 0.5 wt% concentration of Orox PK, the IP was about 5 fold higher (2.7 h) than the original one. With 0.5 wt% Naugard P and DTBHQ provided IP of 1.34 h and 0.98 h, respectively. Thus, none of the antioxidants produced sufficient inhibition to pass the lower US specification of 3 h.

5.5. Canola based biodiesel

Yang et al. [88] investigated on canola-based biodiesel, which they collected from commercial sources. They studied the effect of currently used storage tank materials e.g. steel, aluminum along with copper and lead at varying concentrations in biodiesel. They found that at 0.5% (mass/mass) of metals in biodiesel there was a sharp drop in IP. After that with the increase in metal concentration, the catalytic effect of metals on IP was almost unaltered. Lead and copper showed strong catalytic effect, but aluminum and steel did not show significant catalytic or inhibiting effects. They mixed varying concentrations of PY (50–500 ppm) in 5% (mass/mass) copper and lead adulterated sample as well as in the pure biodiesel sample. It was found that, though initial IP of pure biodiesel was 5 h, it dropped almost to 0 h after adulteration. On the other hand, about 50 ppm of PY increased the IP of pure biodiesel to 10 h. For metal spiked samples, the EN specification is only satisfied for PY antioxidant with an amount of 100–200 ppm.

Focke et al. [98] investigated the influence of three different types of antioxidant on canola-based biodiesel with initial IP of 6.85 h. The added antioxidants were of phenolic (DTBHQ), phosphite (Naugard P) and amine (Orox PK) types (Table 2). They found both DTBHQ and Orox PK increased the IP further. With the increased concentration, IP increased almost linearly for both the cases. However, addition of Orox PK up to 0.5 wt% resulted in pro-oxidative effect i.e. decreased IP. The possible cause of this effect was intricate antagonistic interactions among the synthetic antioxidants and natural antioxidants already present, as explained by them.

5.6. Palm based biodiesel

Serrano et al. [110] conducted the study to observe the influence of effect of four different commercial antioxidants at 1000 ppm and two different purification step on palm based biodiesel as described in Section 5.1. They observed both citric acid and water washed biodiesel met EN 14214 specifications. However, higher IPR was observed for non-stabilized citric acid washed samples when subjected to storage. All the antioxidant were able to meet EN 14214 standard after 6 months regardless of washing step with AO3 displaying the best protection. In another study, Serrano et al. [100] explored same feedstock with same antioxidants at varying concentration and same purification step as described in Section 5.1. All the antioxidants provided good stabilization above 250 ppm with AO3 having greatest result regardless of purification process.

Sarin et al. [133] also conducted the study to observe the influence of various metallic contaminants on the stability of Palm methyl ester (PME). They also doped the PME with various antioxidants to ameliorate the OS. Neat PME exhibited an IP of 9.24 h, which met minimum limits of both ASTM D6751 and EN14214

specifications. Various transition metals namely iron, nickel, manganese, cobalt, and copper, commonly found in metallic containers (as metal naphthenates) were mixed at varying concentration with PME samples. Copper exhibited the strongest catalytic effect on PME. Other metals also had a strong negative influence on the IP. Only 2 ppm of both copper and cobalt decreased IP drastically with reduction of IP to below 3 h. Authors also found that IP values remain almost constant when metal concentration was increased beyond 2 ppm. They choose this level of metal concentration for antioxidant dose optimization. Different antioxidants e.g. BHT, BHA, OBPA, and TBHQ were used at different concentrations. The authors showed that, as the adding amounts of antioxidants are increased, the metal contaminated PME also became more stable. Among the used antioxidants, TBHQ had the strongest beneficial effect on OS. For iron and nickel contamination a min. of 50 ppm; for manganese a min. of 100 ppm, and for cobalt and copper a min. of 150 ppm is required to meet EN 14214 specification.

Liang et al. [118] conducted the study to observe the influence of antioxidant addition on distilled palm oil methyl ester (DPOME). They chose the crude palm oil methyl ester (POME) that had an IP of 25 h because it contained 640 ppm of vitamin E (α-T) and 711 ppm of β-carotene. It is to be mentioned that vitamin E is well recognized natural antioxidant, whereas, β-carotene is a type of biological antioxidants [134]. After distillation both of them disappeared which resulted in IP of 3.52 h. They added α-T, BHT and TBHQ at various concentrations. α-T at 1000 ppm was able to meet EN standard. Only 50 ppm of BHT and TBHQ increased the IP to 6.17 h and 8.85 h, respectively. Thus order of effectiveness was TBHQ > BHT > α-T.

5.7. Cottonseed oil based biodiesel

In their research, Fernandes et al. [119] used freshly produced cottonseed oil methyl ester (CSOME) with IP of 4.9 h. They selected TBHQ based on the recommendation of Ref. [131,135,69]. Amount of added TBHQ were 300, 600 and 1000 mg/kg, which resulted in 6.7, 8.4 and 10.2 h respectively compared to IP of 4.9 h without TBHQ. They showed that biodiesel shows linear increment in their oxidative stability with the variation of concentration of antioxidants.

Tang et al. [121] studied the usefulness of several natural and synthetic antioxidants, e.g. α-T, BHA, BHT, TBHQ, Ionol BF200 (IB), PG and PY to ameliorate the OS of cottonseed oil (CSO) based biodiesel at changing concentration between 250 and 1000 ppm. Commercially available CSOME with initial IP of 6.57 h was used here. The order of effectiveness for CSOME was TBHQ > PY > PG > DTBHQ. The rest did not produce significant increase in IP. TBHQ had demonstrated the utmost effect on its oxidative stability, attaining around 30.2 h at 1000 ppm.

5.8. Safflower based biodiesel

Xin et al. [117] conducted the study to determine the effectiveness of PG with concentrations from 0 to 5000 ppm on highly unsaturated (89.1% unsaturation) safflower methyl ester. The initial IP was only 0.86 h because of having lesser natural antioxidant content (104-ppm tocopherol) in addition to their higher unsaturation chain structures. With the increasing concentration of PG, the IP increases. However, its effect is well pronounced when the concentration is less than 1000 ppm. In case of above 1000 ppm, the tangent of induction period vs. concentration curve gradually decreases indicating a less prominent effect at this stage.

Besides, in another study, Xin et al. [99] explored the effectiveness of PG and DPD (Table 1) at various concentrations. They exposed safflower biodiesel with initial IP of 0.9 h to supercritical methanol at 270 °C/17 MPa for 30 min and compared it with unexposed one. Sample with PG and exposed to methanol produced better result compared to unexposed PG and DPD doped unexposed and exposed biodiesel.

5.9. Castor based biodiesel

Araújo et al. [136] conducted the study on oxidative stability of castor oil biodiesel using a different technique than the standard method set by EN14112. This method evaluates IP making use of pressure drop within a sample, which is exposed to pure oxygen at working pressure and temperature of 700 kPa as well as 140 °C, respectively. A specific pressure drop determines end of test. They used BHA, BHT, PG and TBHQ at 0 to 6000 ppm. The use of antioxidants obtained stabilization from 6 to15. BHA provided the best result at 2000 ppm. The order of effectiveness was BHA > PG > BHT > TBHQ.

5.10. Croton Megalocarpus based biodiesel

Kivevele et al. [125] conducted the study on the effect of three different antioxidants namely PY, PG and BHA at varying concentration to determine the oxidation stability of methyl ester produced from Croton megalocarpus oil. The initial IP of COME was 4.04 h. Among the antioxidants used, PY and PG displayed higher effectiveness compared to BHA.

5.11. Karanja/Pongamia pinnata based biodiesel

Agarwal and Khurana [124] conducted a study to determine the effect of five different antioxidants namely BHA, BHT, PG, TBHQ and PY at variable concentration on four-month storage stability of Karanja based biodiesel with initial IP of 1.82 h. PY at 500, 700 and 1000 ppm and PG at 700 and 1000 ppm was able to meet EN 14214 specification after 4 months. To increase the oxidation stability they used dry washing method by means of magnesol instead of distilled water washing and successfully increased IP up to 2.74 h.

Das et al. [123] conducted the study about the effectiveness of five synthetic phenolic antioxidants namely PY, PG, TBHQ, BHA and BHT at 100 ppm on oxidation stability of karanja oil biodiesel with initial IP of 2.24 h. Except PY and PG, rest failed to impart sufficient stabilization to meet EN 14214 specification. They also studied long-term storage stability (6 months) using BHA, BHT and PG and found PG to be the best antioxidants. However, they did not present IP results. Instead, they showed lower peroxide values in case of stabilized biodiesel.

Obadiah et al. [38] also studied the effectiveness of five different antioxidants (BHA, BHT, TBHQ, PY and GA) on stability of *Pongamia pinnata* biodiesel with initial IP of 3.17 h. They tested varying concentration and found that PY at 2000 ppm and above and TBHQ at 3000 ppm were only able to meet EN specification. For evaluation of long-term storage, they studied kinematic viscosity and acid value for 12 weeks and 50 weeks according to proposed method in ASTM D4625. Due to higher viscosity of this biodiesel, the samples exceeded the ASTM specifications after 3 weeks of experiment [137]. However, non-stabilized samples deteriorated at much faster rate compared to stabilize one. PY provided the best protection for this biodiesel among the tested antioxidants.

Sarin et al. [122] investigated the effectiveness of BHT, TBP and OBPA at different concentrations in pongamia methyl ester with initial IP of 2.54 h. They found that at least 250 ppm BHT can satisfactorily to meet EN 14214 specification. Based on this finding they used BHT for metal contaminated samples for optimizing antioxidant concentration. Copper had strongest catalytic effect, hence requires maximum concentration of BHT. At least 650 ppm of

BHT was required to meet EN specification for all metal contaminated samples.

5.12. *Terminalia belerica based biodiesel*

Chakraborty and Baruah [126] studied the effect of α-T, BHA, PY, PG, BHT & TBHQ added in different concentrations with biodiesel. Freshly produced *T. belerica* biodiesel has an IP of 3.76 h, which fails to conform to EN standard. 100 ppm of PG and PY; 500 ppm of TBHQ and 1000 ppm of BHT were able to enhance IP up to 6 h. α-T and BHA failed to improve IP to the desired level even at 1500 ppm. The order of effectiveness is PG > PY > TBHQ > BHT > BHA > α-T. They also studied the effect of 1000 ppm of PG, BHT and TBHQ on 12 weeks storage and found that only PG added sample was able to meet EN standard after this period.

5.13. *Linseed oil based biodiesel*

Pantoja et al. [127] studied the effect of BHA, TBHQ and PG at various concentrations on linseed oil biodiesel with initial IP of 2.2 h. TBHQ was the most effective antioxidant in this case. However, below 2000 ppm PG showed better efficiency compared to others.

5.14. *Açaí (Euterpe oleracea) oil based biodiesel*

Pantoja et al. [127] studied the effect of BHA, TBHQ and PG at various concentrations on açaí oil biodiesel with initial IP of 1.5 h. PG was the most effective antioxidant in this case. With the increasing concentration of antioxidant, the IP increased gradually.

5.15. *Recycled cooking oil based biodiesel*

Lapuerta et al. [112] studied the effect of test temperature (110–130 °C) and different BHT concentrations on soybean based biodiesel with initial IP of only 0.77 h. From 3000 to 32800 ppm of antioxidant was required to meet the current EN14214 standard at different test temperatures. Almeida et al. [128] studied the influence of the antioxidant TBHQ on the storage stability of this biodiesel. The selection was based on the recommendation of Refs. [135,131,69]. Samples were prepared using static immersion tests in concordance with the ASTM methodology [138]. 5000 ppm of TBHQ was added to study its effect during the corrosion process using copper coupons. Tests were carried out after five different exposure times. The initial induction periods of neat biodiesel and with TBHQ were 6.79 h and 24.0 h, respectively. The induction time measurements after 24, 36 and 48 h immersion revealed slightly higher values for the TBHQ-doped biodiesel (2.42, 2.04 and 1.76 h, respectively) in comparison with the neat biodiesel (1.32, 0.53 and 0.40 h, respectively). Another important aspect evidenced from this experiment was antioxidant slowed the mechanism of corrosion took place there as the releasing rate of copper during the process of corrosion was substantially lesser for TBHQ doped biodiesel. The TBHQ-doped biodiesel showed quantifiable amount of copper only after 96 h of the corrosion experiment. At the same time, the copper content of neat biodiesel was more than three times higher. Thus, phenolic molecules may work as a corrosion inhibitor through forming a protective film layer on the metallic coupon. They attributed this to production of protective film layer by TBHQ molecules that produced partial blocking of the coupon.

Xin et al. [99] conducted the study to observe the consequence of using PG in case of oxidation stability responses of waste cooking oil based biodiesel produced from traditional alkali catalyzed method and supercritical methanol method. They used two types of production method to demonstrate their effect on peroxide value. Biodiesel produced from supercritical method showed almost zero peroxide value and higher IP.

Loh et al. [94] investigated about the effectiveness of using different types of commercially found natural (Vitamin E) as well as synthetic antioxidants (e.g. BHA, BHT, TBHQ, and PG) on characteristic responses of oxidative stability for the case of used frying oil (palm based) methyl ester (UFOME). The research effort was based on finding out most effective antioxidant and the least amount of concentration for which the oxidation stability could be maintained up to the required value as per standard specification at prolonged storage period. Each antioxidant were added at 100, 250, 500, 750, and 1000 ppm with biodiesel and stored for 5 weeks in a dark room and the temperature is maintained similar to the room temperature. Above 100 ppm, all antioxidants enhanced the IP to substantial levels at zero storage. However, over 5 weeks the storage stability decreases drastically ranging 3–35% compared to initial IP. Nevertheless, the IP still met the EN14214 standard for antioxidant concentration of 500 ppm and beyond for vitamin E, BHT and TBHQ and at 250 ppm and higher for BHA and PG after 5 weeks. They concluded that an antioxidant concentration of ≥ 500 ppm is sufficient to meet the EN specification for prolonged storage. The order of effectiveness of antioxidants for UFOME at 500–1000 ppm was PG > BHA > TBHQ > BHT > vitamin E.

5.16. *Animal fat based biodiesel*

Yang et al. [88] investigated on tallow fat methyl ester, which they collected from commercial sources. They studied the effect of currently used storage tank materials e.g. steel, aluminum along with copper and lead at varying concentrations in biodiesel. They found that there were about 0.5% (w/w) of metals in biodiesels, the catalytic effect of metals on OS was almost unaltered. Noticeably lead and copper showed strong catalytic effect, but both aluminum and steel did not show any significant catalytic or inhibiting effects. They mixed varying concentrations of PY (50–500 ppm) in 5% (w/w) copper and lead adulterated sample. Initial IP of pure biodiesel was 10 h, which decreased to approximately 4 h after adulteration. About 50 ppm of PY was sufficient to reach the EN 14214 specification.

Tang et al. [121] explored the usefulness of several natural and synthetic antioxidants, e.g. α-T, BHA, BHT, TBHQ, ionol BF200 (IB), PG and PY to ameliorate the OS of Poultry fat (PF) based biodiesel at different concentration level of antioxidants between 250 and 1000 ppm. Commercially available PFME was used here which had the initial IP of 0.67 h. The order of effectiveness for PFME with these antioxidants was PY > BHA > BHT > PG > TBHQ > IB. Moreover, PY, BHA and BHT managed to cope with the ASTM specification at 500 ppm whereas, in case of PG, TBHQ and IB it was 1000 ppm. DTBHQ failed to meet ASTM standard even at 1000 ppm. PY as well as BHA at a concentration level of 500 ppm could meet the EN 14214 specification.

In another work, Tang et al. [120] inspected the effectiveness of various natural and synthetic antioxidants like α-T, BHA, BHT, TBHQ, Ionol BF200 (IB), PG and PY at a concentration of 1000 ppm to improve the OS of Distilled Poultry fat (DPF) based biodiesel. The refinement of biodiesel usually removes the paltry components such as glycerides, sterols, and natural antioxidants, retaining the FAME composition. Distillation is carried out mainly due to eliminating the effect of age, oxidative history, and minor components. TBHQ, PY and PG produced best result for distilled one compared to BHA, PY and PG for the untreated ones. They also found that, effect of antioxidant is more prominent on DPF based compared to untreated PF based biodiesel. They attributed this effect on untreated one to absence of natural antioxidants, which makes them more vulnerable to oxidation.

Lapuerta et al. [112] studied the effect of test temperature (110–130 °C) and different BHT concentrations on animal fat based biodiesel with initial IP of 15.88 h. About 1000 ppm of antioxidant

was sufficient to meet the current EN14214 standard at all required test temperatures.

Guzman et al. [66] studied the synergistic influence of TBHQ with PY, PG and BHA on distilled poultry fat based biodiesel and found that 2:1 of TBHQ: PY produced the best stabilization compared to individual antioxidants. However, they found the ratio as 2:1 for TBHQ: BHA produced the best synergy.

5.17. Grease based biodiesel

Tang et al. [121] examined the usefulness of both various natural as well as synthetic antioxidants like α-T, BHA, BHT, TBHQ, Ionol BF200 (IB), PG and PY etc. to ameliorate the OS of Yellow grease (YG) based biodiesel at varying concentration between 250 and 1000 ppm. Commercially available YGME with initial IP of 2.25 h was used here. The order of effectiveness for YGME was PY > PG > TBHQ > BHA > BHT > DTBHQ > IB. For this case, addition of α-T had some adverse effects. PY at 250 ppm, PG at concentration level 500 ppm and that of TBHQ at 1000 ppm improved IP above EN standard. The rest failed to meet EN 14214 standard even at 1000 ppm.

6. Conclusion and recommendations

The following conclusions are obtained from this study on the effect of antioxidant concentration on biodiesels derived from different plant and animal based feedstocks.

1. The influential factors on oxidation stability of biodiesel include fatty acid composition, presence of natural antioxidant, and the storage conditions of fuel e.g. exposure to light and air, temperature, and tank construction material.
2. The impact of the antioxidants strongly depends on the feedstock used for biodiesel production.
3. PY produced the best effect in biodiesel stabilization whenever used because of its higher number of labile hydrogen. However, limited solubility on some biodiesels hinders its application.
4. Except PY the others can be ranked for almost all vegetable oil biodiesels as OBPA ≈ DPD < BHT ≈ BHA < DTBHQ ≈ TBHQ < PG. However, for animal fat based biodiesel the rank differs from earlier one. The rank is BHA ≈ BHT < PG < TBHQ. Amine based antioxidants are not tested yet for them.
5. Synergistic effects of two or more antioxidants found by some of the researchers need thorough investigation.
6. Oxidative stability of biodiesel increases linearly with the concentration of antioxidant to a certain amount. Usually sharp increase in IP at lower concentration (less than 1000 ppm) and that of slight increase at higher concentrations (2000–8000 ppm) has been observed.
7. Purification process (e.g. citric acid solution washing, dry washing with magnesol etc.) performed after production of biodiesel was found to increase the oxidation stability of biodiesel. Citric acid washed samples are found to be more resistant to storage oxidative degradation as well as metal catalyzed degradation. However, this needs further investigation.
8. Distillation of biodiesel helped in removing aging and oxidation stability history of biodiesel. Antioxidants were found to produce more prominent effect on distilled biodiesel that needs more research.
9. Metal deactivators such as citric acid, *N*,*N*′-dialicylidene-1,2-diaminopropane etc. along with antioxidants helped in achieving better stability with low concentration of antioxidants in case of metal catalyzed destabilization.
10. Simultaneous addition of citric acid with antioxidants produces synergistic affect which needs further testing.
11. Addition of amine type antioxidants sometimes results in destabilization because of complex antagonistic interactions amongst the natural antioxidants already present.
12. Corrosion inhibition property of antioxidant TBHQ has been tested for copper and zinc. Further research is required for other metals.
13. Biodiesel exposure to supercritical methanol as well as production using it helps in providing better oxidative stability.
14. Addition of citric acid produces synergistic effect with antioxidants that require further investigation.
15. Small concentration of metal in the antioxidants produces a strong catalytic effect. However, IP value becomes almost constant as the concentration of metal increased beyond a certain limit. Copper, lead and cobalt has the strongest catalytic effect that requires antioxidant treatment.
16. Storage stability of biodiesel produced from newer feedstock needs to be investigated exhaustively.

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